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FINAL REPORT

IODINE COLORIMETER

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Prepared for:

National Aeronautics and Space Administration
Manned Spacecraft Center
Houston, Texas 77058

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SUMMARY

The feasibility of direct spectrophotometric analysis of iodine in water has been conclusively demonstrated. Not only can iodine in pure solution be quantitated with satisfactory precision and accuracy, but also iodine in solution with iodides. This represents a tremendous advantage in the planned application in which rather low levels of the bacteriostatic iodine must be measured in solution with high levels of iodide--a combination which presents formidable problems in standard wet chemical analyses. Further, the spectrophotometric method eliminates any requirement for reagents and reagent-specimen measuring and handling procedures. The method is direct, and requires minimal effort on the part of the operator.

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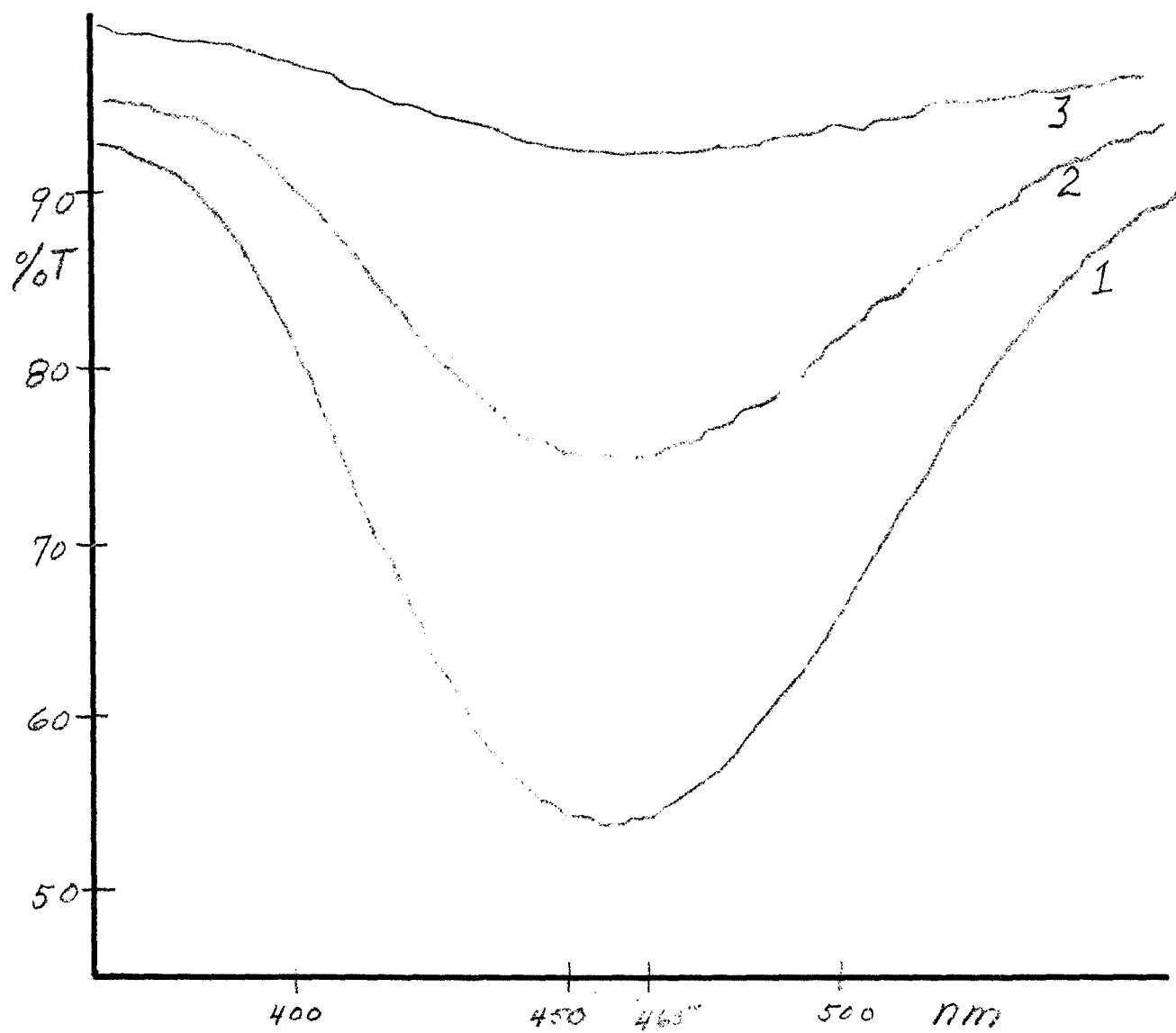
1.0 INTRODUCTION

This report describes the design and development of an instrument for making rapid, accurate measurements of low concentrations of iodine in spacecraft potable water supplies. A direct spectrophotometric technique is used which eliminates the need for additional reagents or complexing agents. This approach offers substantial advantages over the reagent-addition methods commonly used--especially where storage room and reagent degradation (with time) militate against the use of the usual techniques. An obvious advantage of the instrument described here is that of requiring very little effort on the part of the operator to make the aqueous iodine measurement as compared with other methods.

The feasibility of the direct spectrophotometric measurement of aqueous iodine at 0 to 10 ppm levels was established by performing some simple experiments. Since iodine, even in high dilution, imparts a yellow-brown color to water, it may serve as its own indicator. The Beckman DK Spectrophotometer revealed that there is a useful absorption peak at 426 nm. If the solution is quite strong in iodine, or if iodide is also present, two other peaks at 352 and 288 nm appear. Katzin¹ reports that the UV peaks are due to tri-iodide, while solvated iodine is responsible for the 462-nm band. Since iodine has been selected to be used in a similar fashion to chlorine as a bacteriocidal agent for Skylab drinking water, our instrument is optically designed to measure I₂, which recent literature reports to be the most bacteriostatic form of this element². The percent transmission of three different concentrations of aqueous iodine is shown in Figure 1.

¹ Katzin, L.I., J. Chem. Phys. 21, 490 (1953).

² Sullo, Larson, McGurk, Env. Sc. & Tech., 5, No. 3, 240 (1971)



Beckman DK Spectrophotometer. 10 cm path length.
Curve 1: 10 ppm Aq. I_2
Curve 2: 5 ppm.
Curve 3: 1 ppm.

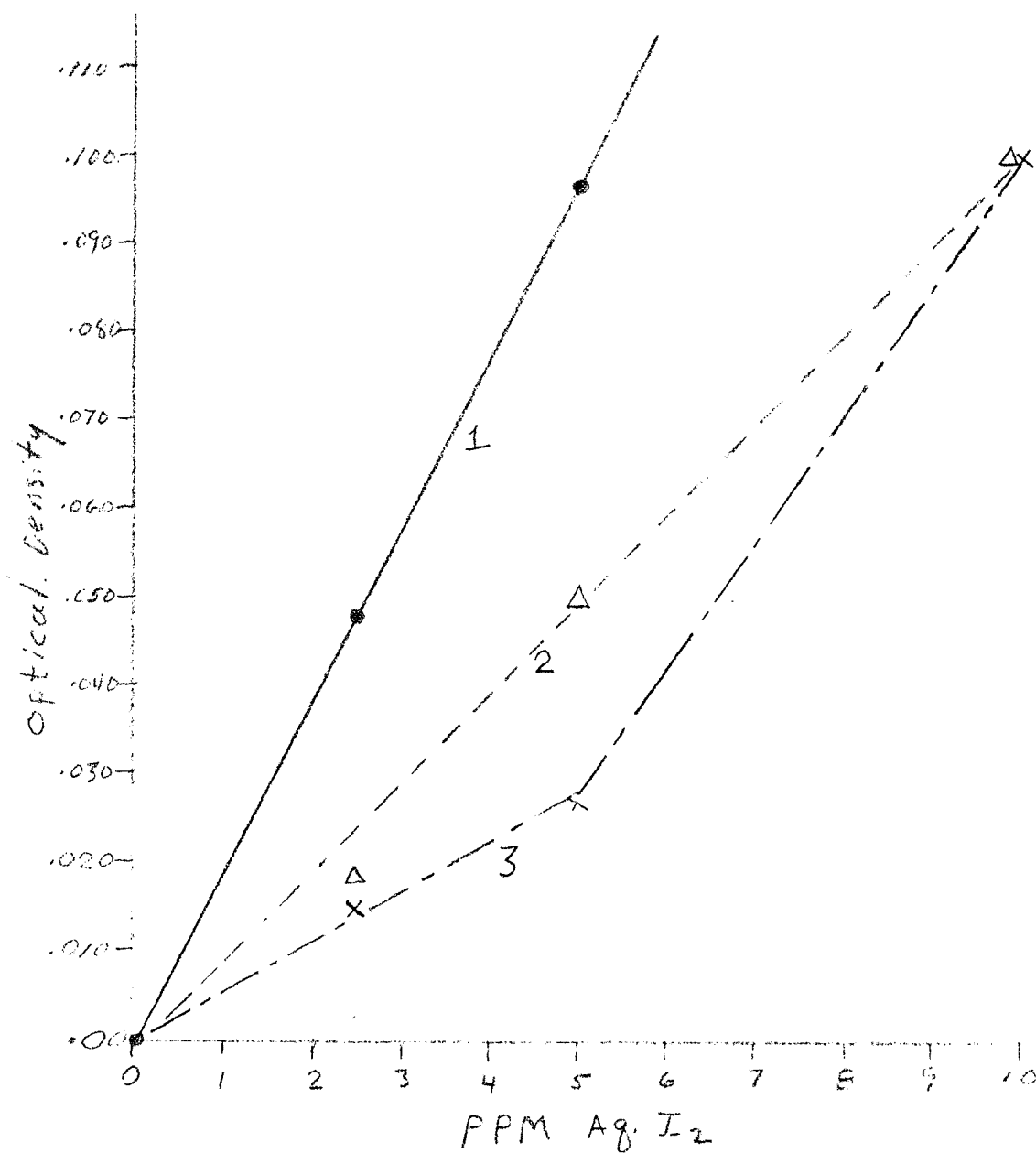
Fig. 1. - - Iodine Absorption Spectra in the 460 nm Region.

2.0 BREADBOARDS

The spectrophotometric studies of aqueous iodine proved the feasibility of using a simple, fixed wavelength colorimeter for measuring 0 to 10 ppm I_2 in water. Moreover, since a small, handheld instrument was desired, we found the 10-cm path length initially used could be shortened to 5 cm without sacrificing the required sensitivity.

Three breadboards, based on the spectrophotometric work, were built. The first one consisted of a series arrangement of a tungsten lamp source, 430-nm filter, 10-cm glass cell, cadmium sulfide detector, a simple circuit, and meter readout. The test solution was made by dissolving 10 mg of elemental iodine in one liter of distilled water. This solution, serially diluted, was used to determine response and sensitivity of the breadboard iodine colorimeter.

This first breadboard showed encouraging results, but suffered from nonlinearity--especially in the 0 to 5-ppm I_2 levels. Breadboard II, with a more appropriate circuit, yielded a linear output over the 0 to 10-ppm I_2 range. It was this breadboard that confirmed the feasibility of the direct spectrophotometric technique for measuring aqueous iodine. Several different detectors were examined using this setup. One, in particular, was so superior to the others that it was used for subsequent work until replaced by a different species of solid-state photosensitive device--the Schottky Barrier Diode. This device had several additional characteristics we desired for our instrument. The previous detectors showed, at best, only 20 percent of their rated sensitivity at our required wavelength of 462 nm. They, also, were adversely affected by light saturation, evidenced by long recovery times. The Schottky Barrier Diode has no memory of exposure to high intensity light, and it shows a broad range of spectral response from 200 to 1000 nm. This desirable sensor was not added to the system, however, until the prototype stage was reached. The breadboards used a Clairex CL 705HL detector. Since the ultimate instrument must be entirely self-contained, a regulated battery power supply was substituted for the bench supply used from the beginning. Figure 2 shows the response of Breadboards I and II to iodine dilutions.



Curve 1: DK Spectrophotometer (reference).

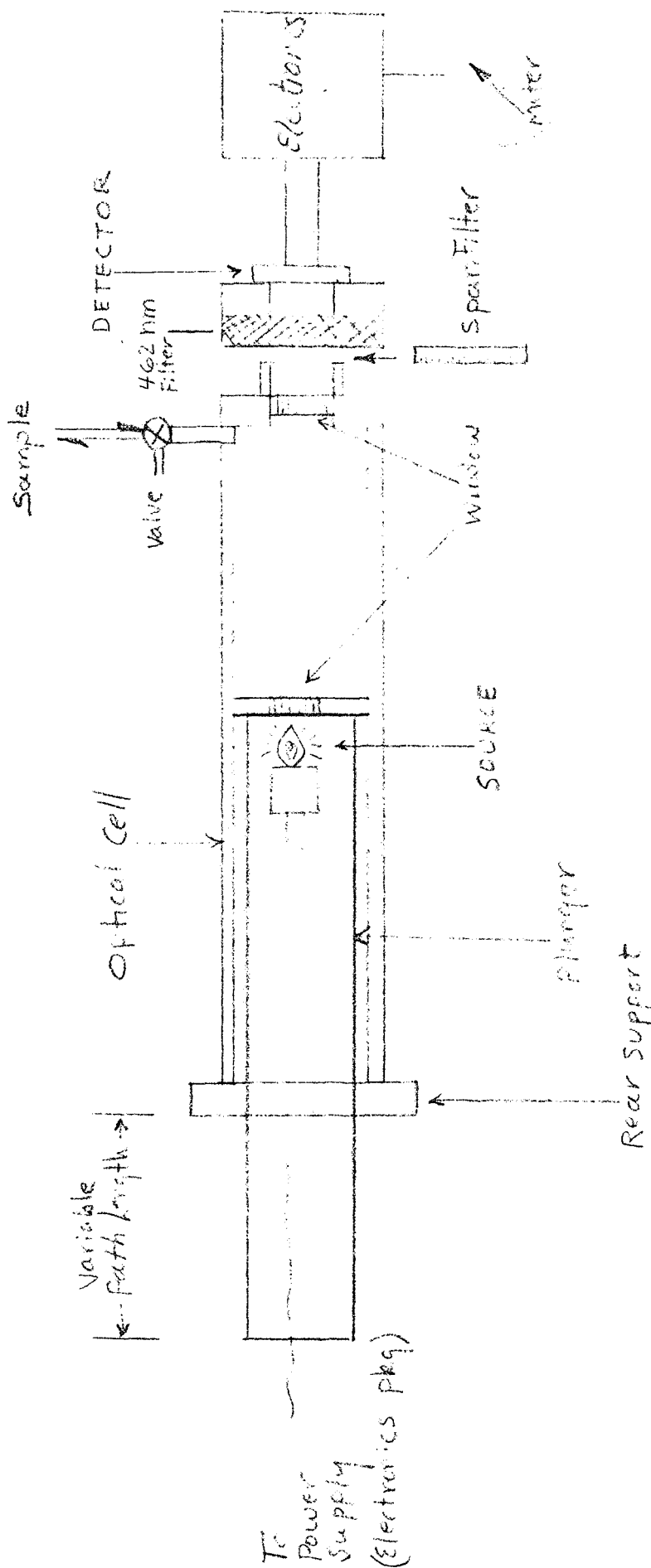
Curve 2: Breadboard II

Curve 3: Breadboard I

Fig. 2. - - Response of Breadboards to Iodine Dilutions.

Breadboard III incorporated a sample-handling system, designed to work in zero gravity. A 30-ml glass syringe barrel was used as the sample cell; the plunger, carrying the light source, provided the means of sample changing. A filter, shutter, and detector at the closed end of the cell completed the optical system. Figure 3 shows a sketch of this system. This is also essentially the arrangement in the prototype.

The performance of Breadboard III was evaluated for overall performance, and its satisfactory behavior provided the basis for design and construction of the prototype. Some test data are shown on page 7. Calibration is done by setting meter zero on iodine-free water and placing a neutral density filter in the light path to set span. Figure 4 shows sensitivity and response of the breadboard for two path lengths.



A 3-way valve at the sample tube permits either distilled water (zero iodine) or sample water to enter or leave the cell.

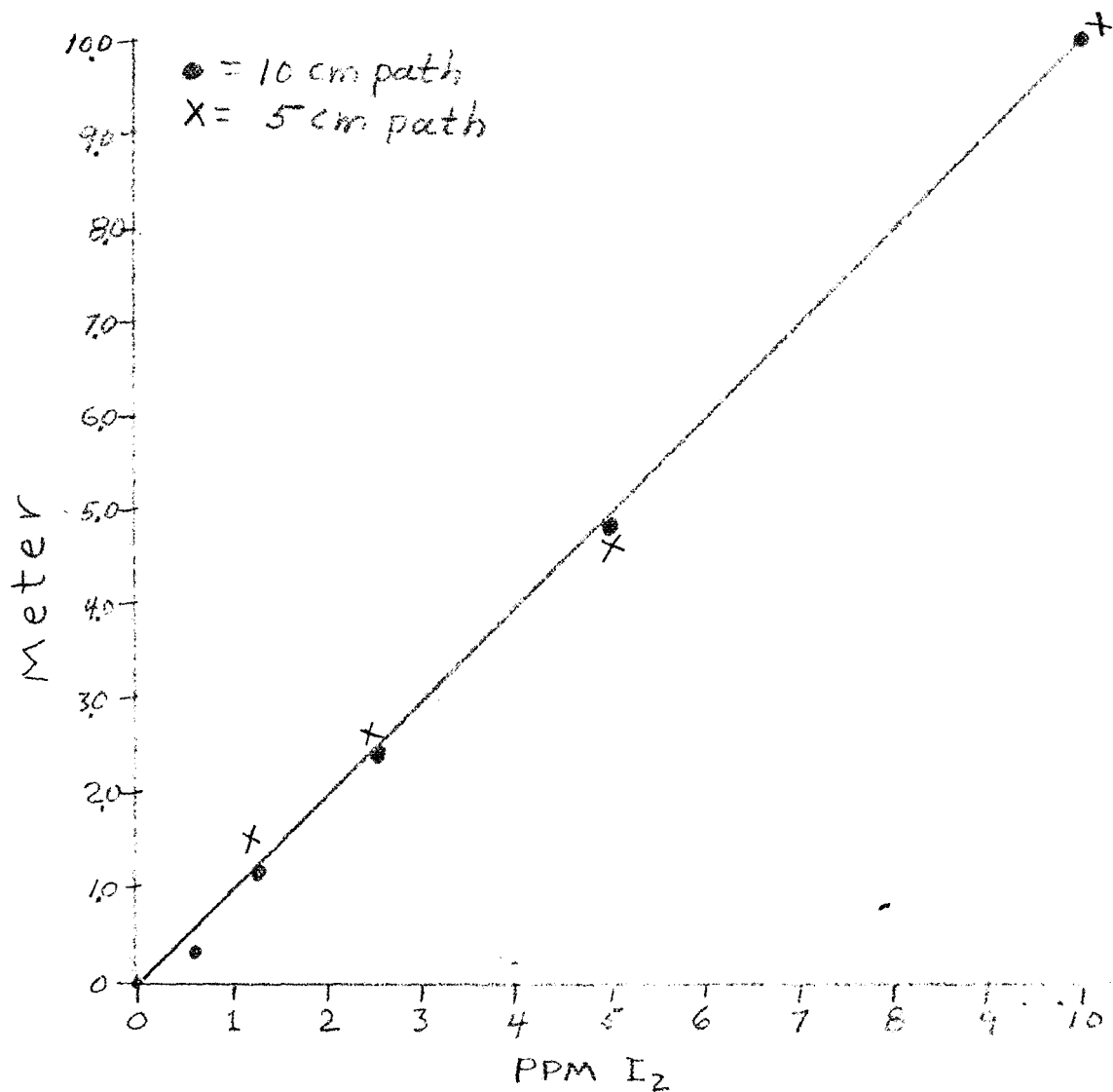
Fig. 3. - - Block Diagram of Breadboard III.

TEST DATA

A precision run on iodine dilutions gave these results. The path length was 5 cm.

Dilution	10 ppm	5 ppm	1 ppm	0 ppm
	10.0	5.4	1.4	-.1
	10.1	5.4	1.1	.1
	10.1	5.7	1.2	-.1
	10.0	5.6	1.4	.2
	10.2	5.5	1.4	.1
	10.2	5.4	1.4	.2
	10.2	5.6	1.3	0
	9.9	5.6	1.3	.2
	10.2	5.5	1.4	.2
	10.2	5.4	1.4	0
\bar{X}	10.1	5.5	1.3	.08
σ	.11	.11	.11	.10
CV	1.09%	2.0%	8.3%	

Note: Since the 5 ppm dilution appeared high, a new one was made and for one observation read 5.0. The DK spectrophotometer confirmed that the first 5 ppm solution was high by about 0.5 ppm.



Sensitivity of the breadboard iodine colorimeter is shown for two path lengths. Since the response at 5 cm path appeared adequate, this length was used for most of the tests.

Fig. 4. - - Sensitivity of the Breadboard Iodine Colorimeter.

3.0 THE CIRCUIT

The electronics for the Iodine Monitor can be broken down into three sections: the lamp regulator, the detector and detector amplifier, and the batteries. A schematic is shown in Figure 5A.

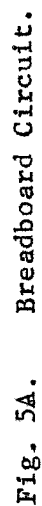
A regulator circuit is required to maintain the voltage excitation for the lamp constant over the life of the batteries and for the duration of each usage. The circuit is composed of a zener diode reference, an operational amplifier, and a power transistor. An extra measure of lamp-drive accuracy is afforded by the use of the operational amplifier.

The zener diode, which provides the reference voltage for the lamp regulator, also provides voltage bias for the detector, a Clairex Electronics Type 705 HL photoconductive cell. The cell, using 5H-type cadmium sulfide material, provides sufficient sensitivity and stability for measurements to below 0.5-ppm iodine.

The detector is connected in a voltage divider arrangement which also includes zero suppression. The reference voltage for the suppression is derived from the lamp excitation, which is, in turn, derived from the same zener diode used for detector bias.

An operational amplifier, with a variable voltage gain of from 7 to 35, amplifies the differential detector signal to 0 to 2.5 volts dc to operate the meter.

Two types of batteries are used. High-current mercury cells are used to power the lamp. The cells, which have a capacity of 14,000-mA-hour, will allow 60 hours of operation at 250 mA of lamp current. The two cells in series provide sufficient voltage to operate the lamp and allow sufficient driver transistor collector to emitter voltage.



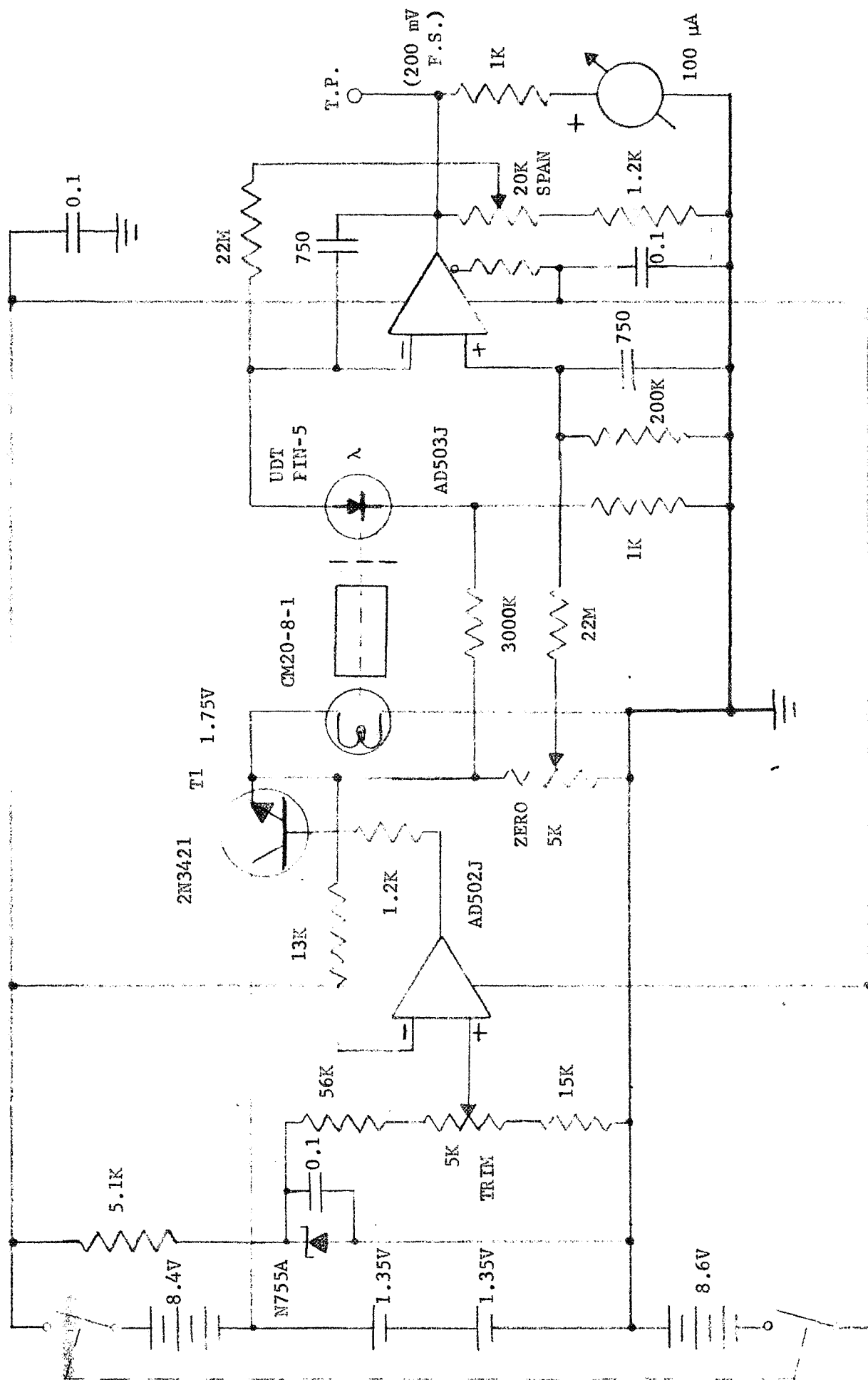


Figure 5B. Prototype Circuit

Low-current mercury cells of 585-mA-hours capacity, stacked upon the high-current cells, are used to supply approximately 5 mA for the operational amplifiers, zener diode, reference voltages, and detector bias.

The main adjustments within the electronics are the zero-suppression control and the span control. A third adjustment, which sets the lamp excitation, should not require readjustment after an initial adjustment.

In place of the cadmium sulfide detector, the prototype uses a PIN/photoconductive junction-type cell utilizing Schottky barrier technology. Operated in the photovoltaic mode, this cell has no dark current. Memory effects are nonexistent and the response time is measured in microseconds. Maximum response is located at 900 nm for this detector, but it still shows about 75-percent response at our wavelength of 462 nm. (See Figure 5B.)

As originally proposed, zero adjustment would be accomplished by utilizing spacecraft iodine-containing water, from which the iodine would be removed by adsorption on a charcoal bed. This would, theoretically, permit recycling of water and thus simplify the operational procedure. Upon investigation, however, it proved impossible to purify the water to the extent necessary to serve as a zero control. This was not due to residual iodine, but rather to finely divided particulate charcoal which proved to be difficult to remove from the water in a reliable manner. Other materials were evaluated for their capability to generate a zero sample, but they also resulted in the generation of unfilterable fines and a meter reading of 2 to 4 ppm.

Accordingly, it was decided to employ pure distilled water without attempting regeneration. This will require the ancillary storage of approximately 200 ml of distilled water in a flexible container. This container will attach to a port in the side of the unit with access to the sample cell through the 2-position valve. After zeroing the meter, this pure distilled water can be discharged into the water supply. This step will also serve to flush any air out of the connecting lines and thus avoid bubbles in the sample.

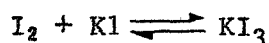
In order to accommodate inter-mission station shut-down requirements and the resultant decreased pressure, sufficient water for each Skylab mission may be canned. Only a few minutes of effort would be required to open a can and attach a new reservoir at the beginning of each mission. Residual water, after each mission, could be discarded in its own bag.

5.0 PROTOTYPE

The essential components of the prototype are shown in Figure 3. Not shown is the rock-and-pinion gear system used to empty and fill the sample cell. Only one-and-a-half turns of the "empty-fill" knob are required to traverse the piston. This results in smooth operation which reduces the possibility of air-bubble formation as the liquids are drawn into the precision-bore pyrex glass sample chamber. The piston head is Kel-F* with a TFE seal. The fluids come into contact only with glass, Kel-F, or TFE. A valve connects the sample cell to "zero-iodine" water or to the sample input port. A spring-return pushbutton inserts a calibration filter into the optical path to set the calibration span point. The assembly shown in Figure 3 is mounted to a sub-base (to maintain optical and mechanical alignment). This and the electronics are enclosed in a clear-anodized aluminum sheet-metal box.

After assembly, the prototype was easily calibrated using serially-diluted aqueous iodine. The straight line calibration curve is shown in part of Figure 6. The effect of foreign substances was briefly examined at the breadboard state (see Progress Report, July 1971). We noted that, unless the interfering substance had a pronounced color, there was negligible effect on the iodine measurement.

However, on learning that the potable water supply would contain iodine and potassium iodide, we investigated this solution in some detail. Figure 7 shows a scan (700 to 350 nm) of the I₂-KI solution for varying amounts of these chemicals. Of interest is the small effect on a fixed concentration of I₂ of 18 to 72 ppm KI at 462 nm. But at shorter wavelengths, the KI effect is pronounced. The I₂ band at 462 nm has vanished, but the 462-nm area still gives a reliable response to I₂ alone. For the I₂-KI response of the prototype, see Figure 6. KI alone shows no absorption across the visible spectrum, but when complexed with I₂



*Registered trademark of 3-M Company

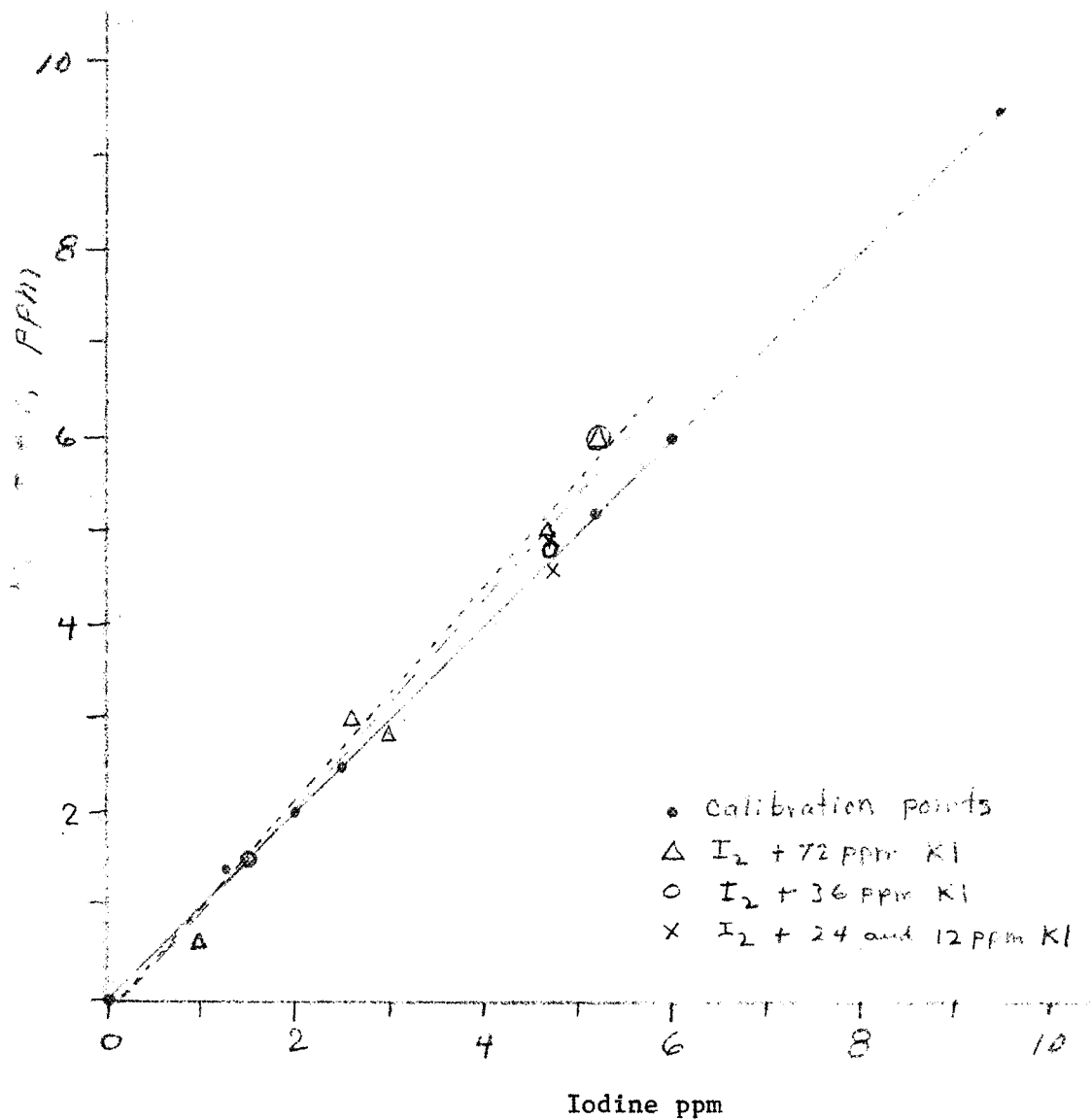


Figure 6. I_2 and KI Solutions-- I_2 Varied from 0 to 9.5 ppm, KI varied from 0 to 72 ppm. Note Linearity of Calibration Curve (I_2 only)

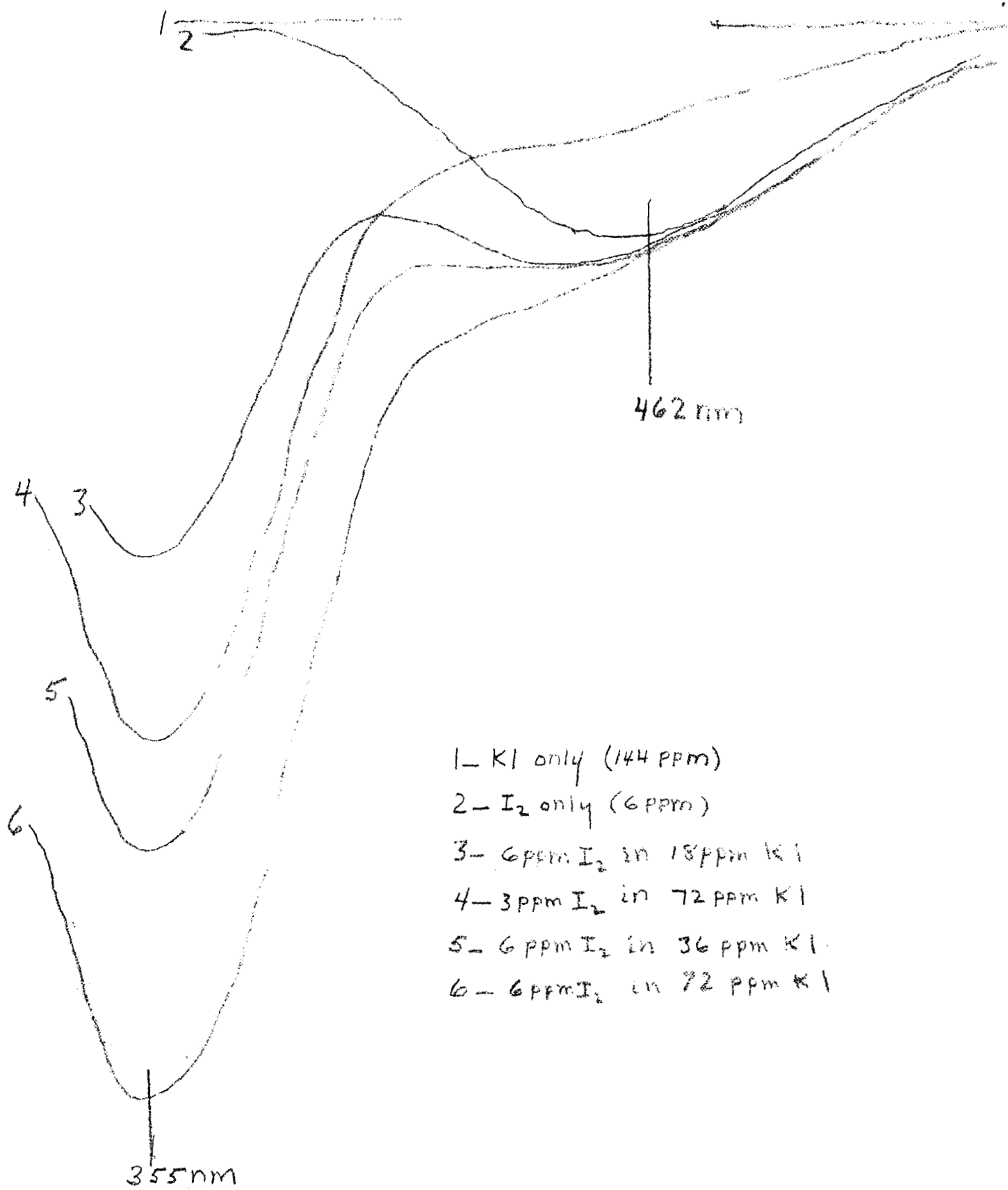


Figure 7. I₂ and I₂-KI Solutions--DK Spectrophotometer

there is a strong absorbance at 353 nm. At this point, one can readily measure small changes in KI_3 concentration--but not in I_2 alone. Since we are interested in measuring small changes in I_2 concentration, our prototype works at the I_2 band of 462 nm.

6.0 RECOMMENDATIONS FOR FLIGHT UNITS

The fabrication and test of the prototype iodine meter has conclusively demonstrated the feasibility of measuring aqueous iodine in water. Although primary emphasis was placed on the evolution of the optical, mechanical, and electronic design during the current phase, analysis of the prototype configuration points out areas where rather minor structural changes would significantly decrease overall dimensions and enhance the portability and storage characteristics. For example, in subsequent flight units, the optical train can be shortened without decreasing the path length by decreasing the length of the lamp housing and the incorporation of the optical filter into the detector face. The circuit board could also be reduced in size now that the electronic design is finalized. An overall size reduction of 50 percent is considered feasible at this point in time.

Other changes in the unit to conform to flight hardware requirements would also be made, i.e., materials, wiring requirements, potting of batteries, etc.

Housing changes would also be made to permit facile interface with the Skylab water supply system and allow ready sampling without fluid loss.